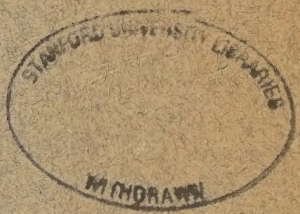
The Development of the Moving Boundary Method for the Separation of Mixtures of Electrolytes, and a Consideration of Its Applicability to the Separation of Isotopes.

by

JAMES FREDERICK WHITE, A.B., M.A.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.



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ABSTRACT OF DISSERTATION

1. What was attempted?

The method of moving boundary was developed as a method for the separation of the isotopes of chlorine. More especially, the attempt was made with non-isotopic mixtures to discover if there was a lower limit of mobility difference below which separation could not be obtained by this method.

2. In how far were the attempts successful?

Substantially complete separations were obtained in the case of iodide and thiocyanate, and barium and calcium. Partial separations were obtained in the case of barium and strontium, and chloride and iodide. This last pair has a mobility difference comparable to that to be expected in isotopes.

3. What new contribution to the science of Chemistry was actually made?

a. The method of moving boundary has been developed to a stage where, in addition to these separations, it has already been proven applicable to the separation of rare earths in this laboratory by another investigator.

b. The tests applied to this method indicate that it gives promise of separating isotopes.

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Introduction

The separation of isotopes is of interest not only to the theoretical physicist, but also to the chemist. To the physicist it offers a chance to study minute differences in atomic structure. To the chemist it offers a chance to study the effect of structure upon those properties of matter used to identify it. Even if a complete separation is not attained the results are still of significance. Various methods have been tried in an attempt to make use of any difference in property in attaining a separation. Lindemann and Aston[1], Mulliken and Harkins[2], and Curie[3] discuss the various methods which have been proposed. Diffusion and distillation seem to be attended with the greatest success, but none of the methods tried have resulted in a perfect separation. From theoretical considerations it seems unlikely that they ever will.

The hope is continually before us, however, that some new means, involving some different property of the atom, will be more successful. The isotopes of the various elements have been detected by methods which took advantage of their identical electrical charge and different mass. But the electrical properties of the atom had not been concerned in the attempts to separate isotopes previous to the consideration of the method of moving boundary. Thus this method offers the possibility of attaining a better separation than the methods previously used, since it introduces a new property. Mulliken and Harkins[2] say that an electrical method such as was used in this investigation is not likely to succeed. Lindemann[4], from theoretical considerations, concluded that there was an appreciable difference in the mobility of isotopes. This confirmed the qualitative reasoning which was the basis of the experiments planned prior to reading this article.

[1] Lindemann and Aston, Phil. Mag., [6] 37 (1919) 523.
[2] Mulliken and Harkins, J. Am. Chem. Soc., 44 (1922) 37.
[3] Curie, J. Phys. et Le Radium, [6] 4 (1923) 381.
[4] Lindemann, Proc. Roy. Soc., Lond., 99A (1921) 87.

THEORETICAL

Isotopic Mobility

On the basis of equi-partition of energy, light particles must have the greater velocity of random heat motion at the same temperature. In a viscous medium, particles having the same volume but different masses, should have velocities of migration, under the same external force, which are an inverse function of their masses. Under these conditions the body with the smallest volume, if of the same mass as the larger bodies, should have the greatest velocity of migration. Lithium has the lightest atomic weight and the smallest ionic volume of the alkali ions, yet it has the slowest ionic velocity under the influence of a given potential gradient. Sodium has the second slowest ionic velocity. The customary reason given for the apparent contradiction of predictions is that the ions are more highly hydrated in the reverse order of their atomic weights. In this manner the ionic mobilities are assumed to conform to the theory. Since isotopes have the same atomic volume[5] but different masses, i.e., different densities, they should have slightly different velocities of ionic mobility.

The calculation of the actual difference in the mobility of isotopes is subject to as great difficulties as any other atomic property. Lindemann[6] has attempted to give a quantitative expression to this value. He concludes that the migration velocity is,

$$v = \frac{l}{2m\sqrt{3kT}} \cdot \frac{2M + m}{\sqrt{M}}$$

and that,

$$\frac{1}{v}\frac{dv}{dm} = \frac{1}{2M} \cdot \frac{2M - m}{2M + m}$$

where,

M = mass of ion
m = mass of water molecule (used as 18 in his calculations)
l = free path

This gives a difference of velocity of 1.7 per cent. for the chlorine isotopes. This entirely neglects hydration and association, which without experimental evidence destroys its quantitative value.

A qualitative expression can be deduced without involving

[5] Soddy, Nature, 107 (1921) 41.
[6] Lindemann, loc. cit.

the constitution of the solvent or the solute.[7] Lewis[8] gives the following expression for the velocity (v) of a charged particle through a liquid under an electric force, when the motion has become steady:

$$Xe = 4\pi a^2 \eta v \frac{1}{l}$$

where,

X = gradient of electrical potential in the liquid
e = charge on the particle
a = radius of the particle
η = coefficient of (self) viscosity of the liquid
l = "facility of slipping" (a linear magnitude) = $\frac{\eta}{\beta}$
β = coefficient of sliding friction of the fluid in contact with tube.

Now,

$$\eta = \frac{1}{3} \rho \lambda u$$

u = molecular velocity (Root Mean Square)
λ = average depth since last impact from which the molecule comes
ρ = density

Therefore,

$$Xe \propto a^2 \rho \lambda u v \frac{1}{l}$$

To a first assumption a^2, λ, and l can be considered as equal for both isotopes. Then,

$$Xe \propto \rho u v$$

Since,

$$pV \propto \rho u^2 \propto T$$

then,

$$Xe \propto T \frac{v}{u}$$

At constant temperature,

$$Xe \propto \frac{v}{u}$$

and,

$$u \propto \frac{1}{\sqrt{\rho}}$$

[7] The author wishes to extend his thanks to Prof. H. W. Farwell of the Department of Physics for aid in deriving this relation.
[8] Lewis, "A System of Physical Chemistry," 2nd Edition, Pg. 336. Taken from Lamb. Phil. Mag., [5] 25 (1888) 52.

This last relation holds for all the particles present in the solution. Thus,

$$Xe \propto v\sqrt{\rho}.$$

In this derivation it is assumed that the viscosity of the solvent is not much affected by the presence of the solute particles, and that the association of the water has no effect. Hydration, if it takes place to the same extent for each isotope, will merely increase the square roots of the densities, and lessen the difference between them. The masses of these particles will be proportional to their densities, since isotopes have the same atomic volume. Chlorine has isotopes of masses 35 and 37. If zero hydration is assumed, the square roots of these quantities are 5.92 and 6.08, respectively. Bjerrum[9] has deduced that the chloride ion has two molecules of water of hydration. Calculations based upon this value give 8.43 and 8.54, respectively, as the two square roots. For the simple ion the difference in square roots amounts to 2.7 per cent., and for the hydrated ion to 1.3 per cent.

Using either assumed constitution of the ion, the mobilities would be proportional to these square roots. The per cent. difference in mobility of the two isotopes would thus be the same as the corresponding per cent. of difference of the square roots.

Moving Boundary

The idea of using the moving boundary was first suggested by Sir Oliver Lodge.[10] Since then it has been used by many investigators for the determination of ionic mobilities or of transport numbers. Kohlrausch[11] considered it theoretically. He reached the same conclusions which were obtained experimentally by others. They found that to keep the boundary sharp it is necessary for the faster ion to precede; also, that the concentrations of the non-similar ions must be in the ratio $C/C' = T/T'$, where C and T represent the concentration and transport number, respectively, of the two ions.

Various corrections and changes have been made in the method. By these means more or less close checks could be obtained where the quantities were known from the analytical methods of determination. The method has passed into disuse because the concensus of opinion seemed to be that it was too uncertain for use with substances whose ionic mobility was unknown. After these experiments were undertaken in this laboratory, MacInnes and Smith[12] used, essentially, the older

[9] Bjerrum, Medd. K. Vetenskapakad. Nobelinst., 5 (1916) No. 16.
[10] Lodge, Brit. Assoc. Rep., 56 (1886) 389.
[11] Kohlrausch, Ann. Phys. und Chem. 62 (1897) 209.
[12] MacInnes and Smith, J. Am. Chem. Soc., 45 (1923) 2246.

method of moving boundary to secure some data they desired.

In its application to the separation of mixed electrolytes the method of moving boundary underwent considerable modi-

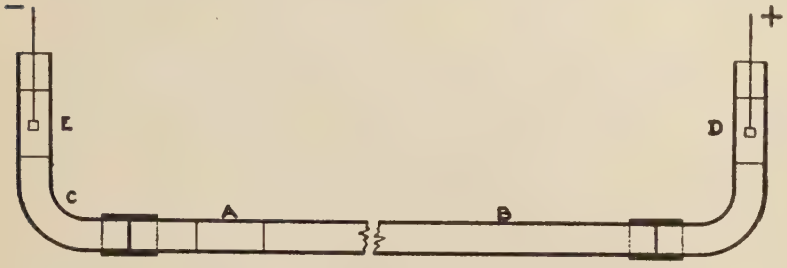

Fig. 1.

Diagram of the Moving Boundary Apparatus

Mathematically the positive direction of x is from right to left.

fication. In the previous use of this method only one boundary was maintained between ions carrying electric charges of the same sign. Here, on the contrary, two boundaries were maintained, so that the ions could neither escape to the front nor to the rear. The method was described by Kendall and Crittenden.[13]

In Fig. 1 the section A contains the mixture to be separated, considered in this discussion as sodium halide. B contains the faster ion which is furnished by sodium hydroxide. C contains the sodium acetate which furnishes the slower ion. All of these are placed in agar to permit of handling without fear of mixing the solutions. The anode vessel, D, contains sodium hydroxide. This will supply the sodium ions to electrolyze through the solution, and will prevent the formation of hydrogen ions. Acetic acid is placed in the cathode vessel, E, to furnish acetate ions and to prevent the formation of hydroxyl ions, which might seriously interfere with the boundary. A. A. Noyes[14] recommended the use of acid and alkali in the electrode vessels to prevent the formation of undesired ions by the discharge at the electrode. The same method can be used for the separation of positive ions by changing the electrolytes and the position of the electrodes relative to the substance to be separated.

The use of two boundaries with the resulting separation of the substances contained between them indicates that none of the existing mathematical considerations of the phenomena of electrolysis are complete in themselves. Kohlrausch[15] devel-

[13] Kendall and Crittenden, Proc. Nat. Acad. Sci., 9 (1923) 75.
[14] A. A. Noyes, Z. phys. Chem., 36 (1901) 63.
[15] Kohlrausch, Ann. Phys. und Chem. 62 (1897) 209.

oped equations for electrolysis involving a moving boundary, but neglected diffusion. His assumption of unchanged ionic velocity with changing concentration simplifies the resulting equation, but is not true at finite concentrations. Planck[16] had previously considered the formation of potential by diffusion. More recently Haskell[17] has considered the diffusion of electrolytes in solutions so dilute that ionization is complete, and in more concentrated solutions where the ions and molecules have different coefficients of diffusion. All of these considerations are involved in the separation of two substances by the method of moving boundary. The omission of any one of these might result in false conclusions concerning the results to be expected from the method.

When two oppositely charged ions are free to diffuse, the faster one has a tendency to precede the slower one, thus establishing a difference of potential which will retard the one and aid the other. Their resulting velocities will be the same. Haskell[17] bases his equations upon this effect. The same equation may be used where there is a potential gradient from an external source. The use of his equation for the diffusion of a partially dissociated electrolyte would greatly complicate the result. It will be assumed that the inclusion of the decrease of ionic velocity with increasing concentration will permit the use of the simpler form of the equation. On this basis the equation which he develops for the number of gram ions passing through a given cross section in a given time will be taken as correct.

$$dN_c = u_c a n_c C \left(-RT \frac{1}{C}\frac{\partial C}{\partial x} - v_c F \frac{\partial E}{\partial x}\right) dt \qquad (1)$$

for the cations, when,

dN = number of gram-ions passing a given cross section in time dt
u = velocity when the force acting upon one gram ion is unity
a = cross section
n = number of mols of ion yielded by the dissociation of a molar weight of the electrolyte
C = concentration of the salt in mols per liter
nC = concentration of ions per liter
R = gas constant
T = absolute temperature (can be considered constant)
v = valence of ions (a constant)
F = the faraday (a constant)
E = electrical potential

The subscript $_a$ refers to the anion, and $_c$ to the cation. In a uniform cylindrical tube these quantities will be considered

[16] Planck, Ann. Phys. und Chem. 39 (1890) 161.
[17] Haskell, Phys. Rev., 27 (1908) 145.

uniform in any cross section. The axis of the tube will be taken as the co-ordinate x, which is positive in the direction of motion of the cation. The potential gradient thus becomes $-\frac{dE}{dx}$.

The change in ion content of the volume bounded by the planes x, and x + dx in the time dt will be,

$$\frac{dN_c}{dt} - \left(\frac{dN_c}{dt} - \frac{\partial}{\partial x}\frac{dN_c}{dt}\,dx\right)$$

or,

$$-\frac{\partial}{\partial x}\frac{dN_c}{dt}dx = a\,dx\,\frac{\partial C}{\partial t} \qquad (2)$$

For the positive ions, substitution of (1) in (2) gives,

$$\frac{\partial C_c}{\partial t} = -\frac{1}{a}\frac{\partial}{\partial x}\left[u_c\, a n_c C\left(-RT\,\frac{1}{C}\frac{\partial C}{\partial x} - v_c F\,\frac{\partial E}{\partial x}\right)\right]$$

$$= \frac{\partial}{\partial x}\left[u_c\, n_c RT\,\frac{\partial C}{\partial x} + u_c\, n_c\, C v_c F\,\frac{\partial E}{\partial x}\right] \qquad (3)$$

Similarly for the negative ions

$$\frac{\partial C_a}{\partial t} = -\frac{1}{a}\frac{\partial}{\partial x}\left[u_a a n_a C\left(-RT\frac{1}{C}\frac{\partial C}{\partial x} + v_a F\,\frac{\partial E}{\partial x}\right)\right]$$

$$= \frac{\partial}{\partial x}\left[u_a n_a RT\,\frac{\partial C}{\partial x} - u_a n_a C v_a F\,\frac{\partial E}{\partial x}\right] \qquad (4)$$

For the positive ions this gives on differentiation,

$$\frac{\partial C_c}{\partial t} = n_c R\,T u_c\,\frac{\partial^2 C}{\partial x^2} + n_c RT\,\frac{\partial C}{\partial x}\frac{\partial u_c}{\partial x} + n_c v_c F\,u_c\,\frac{\partial E}{\partial x}\frac{\partial C}{\partial x}$$

$$+ n_c v_c FC\,\frac{\partial E}{\partial x}\frac{\partial u_c}{\partial x} + n_c v_c F\,u_c C\,\frac{\partial^2 E}{\partial x^2} \qquad (5)$$

Similarly for the negative ions,

$$\frac{\partial C_a}{\partial t} = n_a R\,T u_a\,\frac{\partial^2 C}{\partial x^2} + n_a RT\,\frac{\partial C}{\partial x}\frac{\partial u_a}{\partial x} - n_a v_a F u_a\,\frac{\partial E}{\partial x}\frac{\partial C}{\partial x}$$

$$- n_a v_a FC\,\frac{\partial E}{\partial x}\frac{\partial u_a}{\partial x} - n_a\, v_a F\,u_a C\,\frac{\partial^2 E}{\partial x^2} \qquad (6)$$

For the separation of negative ions $\frac{\partial C_c}{\partial t}$ is not important, except that the concentration of cations present at any point must bear the proper relation of electric charge to the concentration of anions. Each negative ion constituent will have its own equation of the form $\frac{\partial C_a}{\partial t}$. The sign of $\frac{\partial C}{\partial x}$ will depend

upon whether the concentration increases or decreases with increasing x. In Fig. 1, at the boundary BA, $\frac{\partial C}{\partial x}$ is negative for the hydroxyl ions, and positive for the halide ions. At the boundary AC, $\frac{\partial C}{\partial x}$ is negative for the halide ions, and positive for the acetate ions. The halide segment will thus show all the changes of sign which result at either boundary. Thus the signs and effects of each term will be considered more fully only for this section.

The halide segment will move in a negative direction. Thus the boundary BA will be referred to as the forward boundary, and AC as the rear. As previously noted, $\frac{\partial E}{\partial x}$ will always be negative. Mobility is not directly a function of x. The relation is valid through the relation between concentration and x, as follows,

$$\frac{\partial u_a}{\partial x} = \frac{\partial u_a}{\partial C_a} \frac{\partial C_a}{\partial x}.$$

Experimental data (see Table 2) shows that $\frac{\partial u_a}{\partial C_a}$ will always be negative. $\frac{\partial C_a}{\partial x}$, as noted, will be positive at the forward boundary, and negative at the rear. $\frac{\partial^2 C}{\partial x^2}$ changes in sign depending upon whether the curve is concave or convex downwards, being negative or positive, respectively. A similar variation occurs in the case of $\frac{\partial^2 E}{\partial x^2}$. At the points of inflection these terms become zero. In Table 1 the signs of these terms are given in the order of their occurrence with increasing x, i.e., from front to rear of the boundary. The signs given include the sign of the term in equation (6) and result from the substitution of the signs of the individual factors in each term. The resulting signs show whether the term tends to give increased or decreased concentration at a given point with increasing time.

Table 1

Signs of the Terms in Equation (6)

Term	1	2	3	4	5
Forward Boundary	+, 0, —	—	+	—	+, 0, —
Rear Boundary	—, 0, +	—	—	+	+, 0, —

The first term indicates the effect of diffusion resulting from the non-uniformity of the concentration gradient. This is the only effect usually considered in connection with diffu-

sion. The second term shows the effect upon diffusion of the change in ionic mobility with concentration. At the boundary the concentration changes from 0 to 0.1 N with respect to the ions being considered, e.g., according to Kohlrausch and Holborn[18] the mobility of the chloride ion at these concentrations is 65.9 and 56.5 $\times$ 10^{-5} cm./sec., respectively. Thus the tendency is to decrease the concentration more rapidly than shown by the first term.

The remaining three terms concern the electric field. The third term in equation (6) shows the change of concentration at a point due to the movement of the boundary under the influence of the electric field. The fourth term shows that the increase of mobility with dilution modifies this movement. Considered as a volume phenomena the whole boundary does not have the same velocity, since under the same potential gradient the less concentrated portion has the greater velocity. Considering the boundary as a volume introduces the possibility for the ions each to influence the conditions for the other. This would affect the potential gradient. There might also be irregular ionic mobility such as Schneider and Braley[19] found in mixtures of sodium and potassium salts. Neglecting these last two possibilities, the tendency at the forward boundary would be to decrease the slope of the concentration gradient. At the rear boundary it would tend to steepen the slope of the concentration gradient. Mathematically this is also a decrease in slope as it lies in the second quadrant.

The fifth term, giving the rate of change of the potential gradient, is chiefly concerned with the boundaries. When the concentration of positive and negative charges in any section is equal, the potential gradient through that section is uniform, which makes this term zero. Without current a contact difference of potential exists at each boundary. Planck[20] attributes liquid junction potential to the diffusion of the ion of greater mobility across the boundary in quantities too great for electrical neutrality. Since the negative ions of greater mobility are on the side of the boundary toward negative x, in passing across the boundary in the positive direction the potential must decrease. The method of changing from this condition to the steady state under an external electric field, and the exact form of the potential function within the boundary, is unknown. It should be noted, however, that under the conditions of the experiments, the potential gradient within the boundary is very much steeper than elsewhere, as indicated by this liquid junction potential.

If one of the faster forward ions lags behind and attempts to

[18] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898) Pg. 200.
[19] Schneider and Braley, J. Am. Chem. Soc., 45 (1923) 1121.
[20] Planck, Ann. Phys. und Chem., 39 (1890) 161.

cross this boundary it will be returned to its own region. If, on the other hand, the slower rear ion attempts to cross this boundary, its velocity will be increased. It will quickly pass through the boundary toward the region of the faster ion. But the potential gradient is less in this region than where the slower ion exists by itself. The ion which has passed through the boundary cannot remain permanently in the region of the faster ion. Neither can it pass back through the boundary to the region from whence it came. All such ions will thus have a tendency to collect, between the boundary and the region of the faster ion, at a place where the potential gradient enables them to move with the average velocity of the other ions in the tube. As these slower ions accumulate at this place a new boundary between the two kinds of ions will form, with an accompanying liquid junction potential. All of the faster ions will disappear from the place of the original boundary. The result will be a gradual adjustment of potential gradient as it keeps pace with the changing ionic composition.

In the preceding discussion the segment has been tacitly assumed to be homogeneous, i.e., to contain only one substance. This is not the condition when the method of moving boundary is used to produce separations. Application of these principles to the case of the isotopes of chlorine will serve as an illustration of a mechanism by which separation may be supposed to be possible. At first the concentration gradient for both isotopes is infinite. But with the same force the velocity of diffusion of the two isotopes will be different. Owing to the lower concentration present, the concentration gradient of the heavier isotope will decrease more rapidly with time than that of the lighter one. This will tend to make the velocity of diffusion still slower. The rate of change of mobility is probably very closely the same for both isotopes. This would therefore tend to increase the velocity of the heavier isotope to a slightly greater extent than that of the lighter one. Diffusion will therefore cause the lighter isotope to travel farther from the center, both to the front and to the rear. The separation of gaseous hydrogen chloride by diffusion by Harkins and Hayes[21] tends to confirm this picture of diffusion of the chloride ion in solution.

When this segment is placed in an electric field, there are additional effects operating to produce separation. At the forward boundary the greater velocity of the lighter isotope, and the slight relative increase in velocity of the heavier isotope due to its greater rate of dilution, will operate to increase the same effect as resulted from diffusion. At the rear boundary, since the lighter isotope will have the greater velocity toward the main body of the chloride, these effects will tend in the opposite direction than those of diffusion. Until

[21] Harkins and Hayes, J. Am. Chem. Soc. 43 (1921) 1803.

the variable conditions have been evaluated, or standardized, it cannot be decided whether diffusion or electrical mobility will predominate.

At the forward boundary the chance of an ion of the lighter isotope entering the region of high potential gradient is greater than the corresponding chance of an ion of the heavier isotope. Thus the new boundary between chloride and hydroxide which the fifth term of equation (6) is helping to establish will contain an even larger proportion of the lighter isotope than the boundary previously existing. As time passes a boundary will be established between the chloride mixture and this accumulation of the lighter isotope. Boundary conditions at the rear will aid in forcing the lighter isotope to assume a greater velocity than the heavier isotope. The separations obtained by the method of moving boundary between substances of varying differences of mobility show that the portion near the rear boundary is composed only of the substance of smaller mobility. This indicates that the tendency of diffusion is overcome by the impressed potential. If this were not the case the forward portion would contain the pure substance of greater velocity, while the rear portion would still be a mixture of both. But both substances in analogous non-isotopic mixtures can be obtained in the pure form by spectroscopic analysis in the expected portion, as shown later in this article.

There will be a certain amount of diffusion between the section of pure isotope and the central mixture. But until the separation becomes marked the concentration gradient will be very slight. Since the sharpness of the boundary depends to such marked degree upon the differences in potential gradient between the various portions of the solution, the temporary boundaries established between the mixture and the pure isotope will be volume, rather than plane, phenomena. The final boundary obtained when the isotopes have been separated as thoroughly as possible, probably will not be as sharp as those at the ends of the segment. These predictions cannot be verified until the potential gradients, and equilibrium concentrations at the boundary, have been determined for various pairs of ions of different variations of mobility. It seems scarcely possible that, in the processes which formed the elements in their existing isotopic proportions, forces were present to adjust conditions in such a way as to nullify completely the forces tending to produce separation by means of the moving boundary.

EXPERIMENTAL

Selection of Materials

The moving boundary has been previously used in the determination of transport numbers and ionic mobilities. In some of the experiments a jelly of gelatin or agar was used to prevent mixing, in others it was avoided because of its unknown effect upon the results. When the moving boundary is used as a means of separation the samples must be taken without any mixing at the conclusion of the experiment. The use of a jelly, as in these earlier experiments seemed most promising. Gelatin and agar are the commonest jellies, and seemed most suited to the conditions of the experiment. Gelatin melts at a much lower temperature, is more difficult to prepare, and is supposed to have greater chemical activity, than agar. For these reasons agar was used first with such satisfactory results that gelatin was never tried. Since agar does not stick to glass as gelatin does, the experimental procedure as finally developed was much simpler than it could otherwise have been.

Small quantities of agar in pure water cause a firm jelly. The literature on the subject is not entirely in harmony but indicates that the various salts have a great effect upon the firmness of the jelly. A 4-5 per cent. agar jelly was found to melt at about 80°. Sodium nitrate lowered this temperature quite markedly. Sodium chloride, on the other hand, raised it. Throughout the course of the experiments many other salts were tried with a variety of purposes. Sodium acetate, potassium chromate, potassium and sodium iodides, sodium bromide, potassium thiocyanate, barium chloride, calcium chloride, strontium chloride, magnesium chloride, cupric chloride, and zinc chloride gave firm jellies. Potassium dichromate gave a very thick viscous liquid. Acetic acid gave a moderately soft jelly. Some of these electrolytes were tried in high concentrations, 5 M., but most were used at concentrations ranging from 0.1 M to 0.5 M.

None of these fulfil the condition that the ion preceding must have a greater velocity. The chloride ion belongs in the group of the fastest ions aside from hydroxyl. This made it seem imperative to use agar containing this ion. Sodium hydroxide is readily obtainable in greater purity than potassium hydroxide. By its use solutions of approximately the same strength could more easily be made. It was found that concentrations much higher than 0.25 normal refused to set. It is difficult

to prepare a jelly sufficiently firm for the purpose with even these low concentrations.

The mixture of agar and water has to be heated to, or close to, its boiling point. If instead of water a salt solution is used the agar will not dissolve. On the other hand the solid salt, in most cases, will not dissolve in the agar solution. Thus the salt solution was added to the hot agar. In the earlier preparations the mixture was then boiled, but later this was omitted. With sodium hydroxide this procedure results in a black mass. It was found experimentally that cooling the agar before adding the cold sodium hydroxide solution, and placing the mixture immediately in very cold water, gave a satisfactory jelly. This jelly varied from golden to brown, showing that the same action taking place at higher temperatures was operative here to some extent. Throughout electrolysis, which usually required a sample to stand for about a week, the hydroxide agar blackened markedly.

The literature usually refers to jellies containing a relatively high percentage of agar. At first the jellies were made with about 4 gm. agar to 100 cc. water. This gave a very firm jelly, but it was too rigid, as was shown by the great decrease in the number of transverse cracks when the concentration of agar was decreased to 1 gm. per 100 cc. water. This sufficed in the preliminary experiments, but in the larger tube it was necessary to increase the concentration. In most of the experiments 2 gm. per 100 cc. was used.

After selecting the materials the question of purity was considered. For the salts the method in this experiment was considered to be a more thorough means of purification than those ordinarily used. The agar itself might contaminate extremely pure salts. Therefore in most cases the C. P. salts were used. In some subsequent analytical work the sodium chloride was found to be at least 99.95 per cent. pure. (The sample used was recrystallized sodium chloride left by a previous experimenter in this laboratory.) In the first experiments C. P. sodium hydroxide was used. As it was thought that possibly the difficulty in following the boundary was due to the accumulation of the chloride which was an impurity in the hydroxide, sodium hydroxide by alcohol was used in the later experiments.

Commercial agar powder which was known to be impure was used as the source of the jelly. Any very definite information concerning the chemical reactions of the agar was lacking. There was the possibility that the added electrolytes might be removed by the agar during the experiment. The interpretation of the results was greatly hindered by the delays encountered in perfecting the analytical methods. As isotopes were used in most of the earlier experiments, the results are not available. Further consideration of these matters must be delayed until the experimental results have been presented.

Design of Apparatus

When first conceived, it was thought necessary to have a tube long enough for the whole race between the ions. Questions of space precluded this. Instead, a short tube made in sections was used. The path for the ions must be straight; otherwise, in rounding a turn one side of the boundary would get ahead of the other. A horizontal tube eliminated the effect of motion with, or against gravity. Vertical end pieces were necessary in order to permit the electrodes to be placed in solutions rather than in the jelly. Pieces of 1 in. tubing, together with suitable bends, were assembled on the plan later used in the larger tube, and preliminary experiments conducted.

Pieces of 1½ and 2 in. tubing were used in experiments with the agar jelly. Since the concentration of the isotopes had been found to be limited by the sodium hydroxide, the larger tube was preferred as giving the larger samples for analysis. But the jelly exhibited such a tendency to sag that the 1½ in. tubing was selected. Pyrex glass was chosen because of the sudden changes in temperature involved in immersing the tube containing the hot solution in cold water.

Because the experiments lasted for so many weeks it seemed desirable to be able to control the time of renewing the tubes. As the velocity of the chloride segment was sometimes as much as 18 in. a day, three tubes each 3 ft. long were used as the horizontal portion of the apparatus. The bends at the end were 15 in. high in order to allow the agar to be brought well up into the vertical portion and leave room for a considerable volume of electrode solution. The tubes were joined by short pieces of 1¾ in. Gooch tubing. The apparatus as assembled piece by piece was rigidly clamped to a rack so that it could be handled as a unit.

To secure an efficient enough means of cooling, the tubes had to be immersed in water, which was frequently changed. During warm weather a stream of water was kept continually running through the cooling bath.

The electrodes of platinum foil were welded to wires which were sealed into mercury cups. These were carried by rubber stoppers which fitted the open ends of the tube. A large hole in these stoppers provided a gas exit. The electrode solutions were renewed by siphoning off the liquid and adding fresh through a funnel, permanently placed in a third hole in the stopper. Either 240 or 120 volts were immediately available for each tube individually. By throwing the proper switches the ammeter reading for any tube at either voltage could be obtained.

The precautions to be observed in the preparation of the jelly were of continual growth. The process was reduced to a routine at an early date. Various happenings disturbed the normal course of the work and showed that the early successes in the preparation of the jelly had been due to a fortuitous combination of circumstances. No great attempt was made to determine or standardize the method accurately. There were so many known variables that it seemed unnecessary to do this since satisfactory results were being obtained without so doing.

For small quantities the powder was weighed, placed in a beaker, half the total volume of water added, and brought to a boil over the Bunsen flame with continual stirring. The proper quantity of salt solution was diluted to make the other half of the volume and added to the hot solution. This method was used in the preparation of the segments to be separated. Since larger quantities of the agar invariably burned, the vessel containing it was placed in a bath of water which was then heated to boiling. It was found that soaking for about a half hour previous to heating increased the ease of solution and gave a good jelly.

The agar was dissolved in some easily measured volume of water, at least half of the total for the solution. The correct volume of the concentrated stock solution of the electrolyte was diluted with water to make the total desired volume, and added to the agar.

Sodium acetate and sodium hydroxide were the two electrolytes used in greatest quantity. The former would form a firm jelly under almost any circumstances. The jelly set so readily that after insuring complete solution of the agar, care had to be taken that it was not too cold when the salt was added or it thickened too much in the beaker. As already noted sodium hydroxide was more of a problem. In order to be certain of a firm jelly the agar could not be below 60° when the cold solution of the hydroxide was added. The upper limit was at least as high as 65°. These conditions were not always sufficient to secure good results. If the agar was not stirred enough while heating, on cooling it would give the appearance of small flakes floating in a liquid, instead of setting. Insufficient heating, failure to cool soon enough, or to a low enough temperature, gave at best a mushy liquid. As far as was ascertained the success or failure, for these reasons, depended entirely upon the judgment of the experimenter.

While the solutions were being made the tubes were prepared. If it was the beginning of a new run the segment containing the sample to be separated had already been placed in the tube. To do this the tube, closed at the end with a

rubber stopper, was placed in a vertical position. The agar solution which had been made by the method for small quantities was poured in until the desired length of segment was obtained, and allowed to set. The apparatus was assembled and filled to well up in the bends with the proper agar solutions. It was then placed in cold water to set, after which the electrode solutions were added, the electrodes inserted, and the current turned on.

It was found that sodium chloride and sodium hydroxide impart optical properties to the agar which are sufficiently different to permit of the boundary being visually followed at times. In the small tubes used in the preliminary experiments the lighter color of the sodium chloride was specially marked. Generally the darkening of the agar due to the previous presence of sodium hydroxide was sufficient to obscure this. The heating effect of the current is greater in sodium acetate than in sodium hydroxide, due to the greater resistance. It was found that by exposing the tube to air for a short time the difference in temperature resulting at the boundary would become appreciable to the hand. This means failed in many cases. Sodium chromate seemed to offer the possibility of a color boundary. Each time it was tried the color faded, while the boundary became hazy and disappeared.

Mr. B. L. Clarke devised a method of roughly measuring the conductivity as a means of locating the boundary. As applied to these experiments a pin was inserted in each side of the rubber connection. The conductivity was measured by a milliammeter, using a small two-cell flashlight battery as the source of current. If sodium hydroxide was present at the joint the reading was 15 to 25 ma. If sodium acetate was present the reading was only 5 to 7 ma. If possible this method was used only to confirm other indications, as it alone was not considered sufficiently accurate to show the difference between the presence of chloride and of acetate. After the tube was opened the presence of hydroxide or acetate could be confirmed by red litmus paper. If it was hydroxide it was turned deep blue, if acetate a very pale blue. The presence of the chloride when the run was brought to a conclusion demonstrated the success of these methods of locating the boundary.

When the segment had reached the third tube the current was turned off and the tube disconnected. The contents of the two tubes through which the segment had passed were discarded, and the tubes cleaned. The tube containing a segment was moved back to the position of the first tube. The apparatus was re-assembled and filled in the same manner as previously. When the run was completed the agar containing the segment was slid out on a clean glass plate. The segment was cut into sections of the desired thickness with a spatula and transferred to watchglasses. Appropriate tests were made

to show exactly which sections contained the desired substance. Since the samples received so many varied treatments after this step, depending upon their composition, further discussion of their treatment will have to be reserved until the individual runs are described.

Preliminary Separations

Before securing the large apparatus it was desired to prove the method qualitatively. This could be done by separating two ions of a known difference of mobility. If the separation was as complete as expected qualitative tests would show the success or failure. Negative ions were chosen as they were most closely allied with those to be used later. The first pair contemplated was iodide and nitrate. But it was found that the sulfuric acid blackened the traces of organic matter present and rendered the interpretation of the test uncertain. Iodide and thiocyanate, as shown in the values in Table 2, have slightly greater mobility differences.

Table 2

Ion Mobility in Water Solution at 18°.

Conc.	I	NO_3	SCN	$C_2H_3O_2$	OH	Cl	$\frac{1}{2}CrO_4$	Br
				Kohlrausch and Holborn[22]				
0	66.7	60.8		33.7	174	65.9		66.9
0.1	57.3	51.4		26.4	157	56.5		57.5
				Landolt-Börnstein[23]				
0	66.5	61.7	56.6	35.	174	65.5	72	67.0

The two sets of data do not agree beyond showing that the difference in mobility between iodide and nitrate is about 10 per cent. That between iodide and thiocyanate is from 16 to 19 per cent., depending upon the method of calculation.

A mixture of 0.1 N total concentration of potassium iodide and potassium thiocyanate was used in two runs. The results of Schneider and Braley,[24] although not published until much later, show the wisdom of using salts of the same metal. Addition compounds of positive ions could not be formed in the

[22] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898) Pg. 200.
[23] "Landoldt-Börnstein, Physikalisch-Chemische Tabellen" 5th Edition (1923) Pg. 1105.
[24] Schneider and Braley, J. Am. Chem. Soc. 45 (1923) 1121.

segment and it is doubtful if they could across a boundary. The first run involved filling the small tube four times, with a total distance of about 5 ft. and a 2 in. segment. A very good separation was obtained. The second run was designed to test the rate of separation. The segment of the same original length as before was passed once through the tubes (about 17 inches.) The segment increased to a length of 3 inches. Thus the length of segment was approximately a little less than 20 per cent. of the distance travelled, or about numerically equal in this percentage to the per cent. difference of mobility. The separation was very marked, although not as complete as before.

Due to the contraction of the agar on setting, and its not sticking to glass, the material could be slid from the tube at the conclusion of the experiment. The front line of the segment was distinct, so that it was possible to cut it into sections about 1 cm. thick. These sections were placed in contact with equal volumes of water. Separate portions of the extract were later tested with ferric chloride and with carbon disulfide and chlorine water. Efforts were made to keep these tests uniform in method so that the relative quantities could be estimated from the results. In Table 3 the sections are numbered from front to rear. In the first run it shows the absence of thiocyanate in quantity great enough to affect the ferric chloride in the front portion, and of iodide sufficient to color the carbon disulfide in the rear, just as would be expected from their mobilities. The decreased intensity of the end sections, more noticeable at the rear, indicates that the boundary of the segment was contained within the sample, thus diminishing the quantity present in the test but not indicating a lower concentration within the segment.

Table 3

Record of Iodide—Thiocyanate Separations

Section No.		1	2	3	4	5
Run 1..	I	Strong	Some	None	None	
	SCN	None	Slight	Strong	Some	
Run 2.	I	Very Strong	Fairly Strong	Faint	None	None
	SCN	Slight	Medium	Very Strong	Very Strong	Faint

The sodium hydroxide used in these experiments seemed to be the chief limitation upon the method. It was thought that possibly barium hydroxide might have less effect upon the agar. The experiment was a failure compared to the use of sodium hydroxide, as the velocity of the segment was much less. The ease with which barium carbonate precipitates from both the hydroxide and the acetate, and the slight solubility of barium hydroxide made the preparation of the agar much more difficult than when the sodium compounds were used.

The proper concentrations of electrolytes to keep the segment of uniform length were found by experiment. No attempt was made to determine the exact concentrations present in the agar either before or after a run. The very evident reaction of the sodium hydroxide with the agar, and the lack of data concerning ionization in solutions of electrolytes in the presence of agar, preclude the possibility of calculating ionic concentrations or even salt concentrations from the quantities added in making the solutions. It is probable that the concentrations at a boundary were in a ratio at least similar to $C/T = C'/T'$, as found in the determination of transport numbers and ionic mobilities. The change in length of the iodide-thiocyanate segment illustrates the adjustment of concentrations which were not originally in the proper ratio. This represented a change in concentration of approximately 33 per cent. MacInnes and Smith[25] secured a concentration change of only 5 per cent. in their experiments. If they had caused their boundary to migrate a greater distance, they probably would have secured a larger adjustment of concentrations.

Halide Separations

It was thought that even though the method of moving boundary might separate substances of a large difference of mobility, with a smaller difference diffusion might nullify the effects of electrolysis. The separation of iodide and thiocyanate showed but little concerning the range of applicability of this method. Isotopes are very difficult to analyze and probably have very nearly the same mobilities. It therefore seemed desirable to test the method on substances of known differences of mobility which could be analyzed more readily.

The other halides are very similar to chloride in mobility. They are also fairly easily detected as a group and individually. Their mobilities decrease in this order: bromide, iodide, and chloride. As will be seen by reference to Table 2, the data is not consistent for the exact magnitude of the differences in

[25] MacInnes and Smith, J. Am. Chem. Soc. 45 (1923) 2246.

mobility. Kaye and Laby[26] give even greater differences, 70, 68.8, and 67.8, respectively. This would indicate an excellent chance to separate bromide and iodide. No matter what length the segment might be, the forward and rear layers of molecular dimensions should soon be purified. This should spread through the segment, so that in time a finite distance should have reached its final composition, within the limits of analysis. To attain complete separation the greater the length of the segment, the longer the time required. This would dictate that the segment be as short as possible. The low concentration of sodium hydroxide, which could be used, made the concentration of sodium halide still smaller, 0.1 N. A segment 2 or 2½ in. in length would give, on cutting into sections, six portions about 1 cm. thick, which would contain sufficient halide to precipitate about 0.1 gm. of silver halide.

Experiments were undertaken to effect a separation of bromide and iodide. The positive portion of the tube was filled with 0.22 N sodium hydroxide in 2 per cent. agar. The segment contained 0.1 N total sodium halide. The negative end consisted of a few inches of 0.2 N sodium acetate. It made no difference whether 1.5 or 2 per cent. agar was used for the last two. The positive electrode vessel was filled with moderately concentrated, 2 or 4 N, sodium hydroxide solution, the negative vessel with acetic acid, 50 per cent., containing a little sodium acetate to give great conductivity. No accurate record of the current was kept. As each run proceeded it decreased, usually from about 0.25 A at first to about 0.1 A. This was due to the increased resistance occasioned by the greater length of acetate.

Eight trials were made, of which two were carried to completion. Jelly which was insufficiently set was responsible for most of the failures. At the conclusion of the experiment the agar was cut into sections and dried. Before drying, a small piece from the edge of each section was extracted with water. A portion of the water extract was tested with nitric acid and silver nitrate. Those sections contained within the segment gave a heavy white precipitate. To the front and to the rear of these there were always some which gave an opalescence. This may have been due to the liquid which filled the space in the tube around the agar. It may have been due to the boundary shading off, instead of being a contact between two planes. Washing the agar with a stream of water did not remove all of the substance causing the opalescence. This would indicate that both reasons operate. To the rear of the halide there appeared a brownish precipitate, evidently from the agar, which seemed to dissolve in ammonium hydroxide. The agar itself gave a brownish precipitate with silver nitrate in ammoniacal solution, but here it seemed that the

[26] Kaye and Laby, "Tables of Physical and Chemical Constants." (1911) Pg. 88.

precipitate changed. The samples gave no such precipitate after ignition. It may be the silver salt of an original component of the agar, or of a decomposition product formed during electrolysis. Those giving heavy precipitates with silver nitrate were saved for analysis. The extracts of these samples were further treated with sulfuric acid and potassium nitrite. The liberated iodine was then extracted with successive portions of chloroform. The bromine was liberated by dilute potassium permanganate and extracted with chloroform. The results gave no indication of the relative quantities present and showed that in no sample was there complete absence of either one.

In preparation for analysis by the Volhard method the samples were dried and fused. The residue was extracted in boiling water and filtered. After acidifying with nitric acid, an excess of N/25 silver nitrate was added. The solution was heated almost to boiling and allowed to stand at least over night. The precipitate was collected and weighed on a Gooch crucible. The combined filtrate and washings were titrated with ammonium thiocyanate, using ferric ammonium sulfate as indicator. High values were obtained for the volume required to precipitate a gram of silver halide. This was evidently due to chloride which had collected from the agar and the other chemicals used. Qualitative analysis of part of the solution from one of the samples showed chloride. A 2¼ in. segment travelled for 30 ft. During this time it was in contact with at least 250 gm. of agar which had contained 125 gm. sodium hydroxide. Evidently this method of electrolysis must be fairly efficient as a means of purification, for the results would indicate a gathering of chloride to about the extent which a conservative estimate would credit these chemicals as containing. The transfer of water from the positive to the negative electrode vessels might carry chloride from the electrode solution of the hydroxide to a region where it would enter the segment. But it hardly seems possible that chloride would travel so far against the current.

If Kohlrausch and Holborn's values for the mobilities of the halogens are correct, instead of Kaye and Laby's as originally used, separation would be doubtful for bromide and iodide in the distance of this experiment (See Table 4). Kohlrausch and Holborn give the difference of mobility as only 0.2×10^{-5} cm./sec. If the halide ions should combine, as Schneider and Braley[27] conclude is the case with the alkali ions, no prediction could be made concerning the relative mobility of any given ion. With three variables and only two factors it is quite possible that the analytical method would fail to detect a separation of any two of the three. Thus this experiment failed to contribute any definite information concerning the possibility of separating these ions.

[27] Schneider and Braley, J. Am. Chem. Soc. 45 (1923) 1121.

Table 4

Record of Halide Separations

Run	Dates	Section length	No. of fillings	Total distance
		Br-I		
23	12/31/23-2/4/24	2¼ in.	5	30 ft.
		Cl-I		
29	3/22/24-4/22/24	2½ in.	5	30 ft.

A mixture of chloride and iodide was next placed in the tube. It was foreseen that the collection of chloride would decrease the results which could be expected. In comparing the results obtained in this case with those subsequently recorded for the alkaline earths, it is necessary to use a common basis. The unit length of run is such that the length of the segment, expressed in per cent. of the length of run, is numerically equal to the difference in the mobilities of the two ions, expressed in per cent. Thus the 30 ft. traversed in this run is about 200 per cent. of the unit length of run.

The samples were fused in a platinum crucible and analyzed as described previously. The results were all displaced toward the chloride value, as would be expected if it were collecting from the material used. They are given in Table 5. The forward sample analyzed gave only about 9 mgm. precipitate, using about 0.9 cc. so that the value is not trustworthy. Qualitative analysis showed that it contained chloride, as well as iodide. The other samples contained iodide as shown by analysis. No attempt was made to identify chloride, other than the indications of its presence from the number of cc. of silver nitrate necessary to precipitate 1 g. of silver halide. The boundary evidently occurs between samples 3 and 4. As a precaution, about half of each solution resulting from the ignition of the agar was saved from the first analysis. When Sample 4 did not give the same value as sample 3, the second portions of these two were analyzed. These values serve as a confirmation of the method of analysis. It was found necessary to add a large excess of silver nitrate, as indicated by the coagulation of the precipitate, in order to be certain of an excess for titration after filtration. This introduced an appreciable error in the silver nitrate equivalent of the ammonium thiocyanate, even though the factor had been determined to ± 0.2 per cent. As the precipitates were small, several about 65 mgm., the precision to be expected agrees with the results.

Table 5

Analysis of Chloride-Iodide Separation

(Showing cc. necessary to precipitate 1 gm. of silver halide.)

Samples from Run 29

2—103.2
3—133.8 and 136.5
4—149.6 and 145.6
8—152.1
9—155.6

Reference Substances

NaCl 171.3 NaI 104.8

Alkaline Earth Separations

After the analysis of the bromide-iodide experiment it was felt desirable to establish the lower limit at which the method of the moving boundary would effect separation, and to estimate the rate at which the separations were attained. Mr. B. L. Clarke had secured separations of the rare earths by use of this method. Sufficient is not known about their mobility to make a statement concerning the percentage difference. The tables of mobilities were carefully examined to select pairs of ions with different mobilities, whose separation could be detected analytically. The remaining common negative ions were eliminated by the difficulties of analysis. Acids cannot be placed in the agar jelly with any success. This eliminated potassium, ammonium, and the others in this range of mobility, because there was no faster ion to precede them. Magnesium, copper, zinc, iron, nickel, cobalt, and cadmium are among the slowest di-valent ions. Lithium is slower. But experience in this laboratory, e.g., chromate in the isotopic experiments, shows that a mono-valent ion will not successfully follow a di-valent ion. Silver reacts with the agar. This leaves the alkaline earth group as about the only ions available. It was found that they give firm jellies. The use of copper as the slow ion forms a boundary which can be readily followed. The mobilities are given in Table 6.

Table 6

Mobilities of Positive Ions in Water Solution at 18°

Conc	K	½Ba	½Sr	½Ca	½Cu
		Kohlrausch and Holborn[28]			
0	65.3	57.3	54.0	53.0	
0.1	55.8	33.8	30.5	29.4	
		Landolt-Börnstein[29]			
0	64.6	55.	51.	51.	46

Since the salt content of the agar had been found to be important a qualitative analysis of the ash was undertaken to learn if there was any substance present which might interfere with the alkaline earths. In most cases group tests only were made. Comparison with the analyses reported by Fellers[30] aided in the identification. Silicon dioxide remains after the extraction following fusion. Iron and aluminum were identified. An alkaline earth was present which was evidently calcium (see analysis of separation 102). Among the negative radicals only sulfate and chloride were detected. Fellers records also magnesium, phosphate, and a trace of iodide, which may be of importance in connection with these experiments. Fairbrother and Mastin[31] found that the sulfate is freed by hydrolysis, even in distilled water. It was realized that this might cause loss of the alkaline earths by precipitation. If any precipitate was formed during these experiments it was too slight to be visible. As no other ions seemed available for these tests the alkaline earths were used to give graded differences of mobility. These experiments were conducted while the chloride-iodide separation was running.

No attempt was made to determine independently the proper concentration of the various salts necessary to obtain the most constant length of segment. Based upon the work of Mr. Clarke with the rare earths, concentrations which were approximately correct were selected. Different combinations were used in each run with about equal success. Potassium chloride was used as the source of the faster ion. Cupric chloride was used to furnish the slower ion and to indicate the boundary. Hydrochloric acid was used in the anode vessel. A paste of magnesium oxide in a mixed solution of mag-

[28] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898) Pg. 200.

[29] "Landolt-Börnstein, Physikalisch-Chemische Tabellen," 5th Edition (1923) Pg. 1105.

[30] Fellers, J. Ind. Eng. Chem. 8 (1916) 1128.

[31] Fairbrother and Mastin, J. Chem. Soc. Lond. 123 (1923) 1412.

nesium and cupric chlorides was tried in the cathode vessel. It was hoped that the magnesium oxide would prevent the liberation of chlorine and trap any hydrogen ions which might try to enter the agar. This set to a very hard mass which let almost no current pass. Attempts to prepare cupric hydroxide resulted in the formation of a black substance which was so slightly soluble in acids as to give little promise of trapping the hydrogen ions. The tube was running during these attempts to prepare a suitable base. There was but little chlorine liberated in the room, most apparently going into solution in the cupric chloride, to judge by the rate of bubbling at the two electrodes. As far as could be detected there was no disturbance of the boundary due to hydrogen ions formed by reactions in the cathode vessel. Thus cupric chloride was used as the electrode solution without further attempts at change.

The pairs of alkaline earths were tried in order of decreasing difference of mobility (see Table 7). The results with calcium and strontium were inconclusive. A serious mechanical accident shortly before the completion of the electrolysis might account for the uniformity found throughout the segment. The separation of chloride and iodide established limits for the applicability of the method lower than the 3 per cent. difference between the mobilities of these ions. As the experiments were primarily undertaken to determine the limits of the method if it failed to separate chloride and iodide, a repetition with calcium and strontium was unnecessary.

Table 7

Record of Alkaline Earth Separations

Run	Dates	Distance	Per cent difference mobility	Per cent of unit run	Section Length
101 Ba-Ca	3/25/24-4/3/24	81 in.	12	370	2⅝ in.
102 Ba-Sr	4/5/24-4/9/24	40 in.	10	200	2 in.

When the segment was cut into sections flame tests were made to locate the various substances. This was possible as the colors appeared in succession. The chosen samples were set aside until the use of the spectroscope had shown that gravimetric analysis was unnecessary. The lines from the pure alkaline earths together with such other lines as could be obtained from other substances were used in plotting a calibration curve. Most of the lines appearing in the alkaline

earth spectra could thus be identified. Observations were made upon each section obtained from the segment, with special reference to the lines which had shown themselves to be characteristic of the various elements.

The greatest difficulty seemed to be in securing sufficient intensity of flame. The lines used as a basis of comparison in most cases are fairly closely associated. The instrumental errors were probably the same each time, approximately, as evidenced by the regularity of the results. Even though the ultimate precision of spectroscopic analysis was not attained, the absence of a given element indicates that much smaller quantities were present than could probably be detected by gravimetric analysis. But the spectroscope fails to show the difference between traces due to impurities and large quantities.

The samples from Run 101 were cut about 5 to 7 mm. thick in anticipation of gravimetric analysis. The samples from Run 102 were cut as closely to 5 mm. thick as could be readily estimated. In this way it was determined that the short segment had aparently increased slightly in length.

Table 8 shows the flame tests and spectroscopic lines obtained from the various samples. The wave-lengths of the lines used to identify the elements are given in Table 9. The broad diffuse green band containing several lines, and the strong green line, are most characteristic of barium. Calcium gave a red and green band of great intensity. After the green band of calcium disappeared the strong barium line would appear about where the middle of the band had been, if both were present. Strontium gave a large number of lines and bands in the red, a very persistent orange line which appeared late, and a line in the blue. Frequently on dipping the wire in hydrochloric acid to clean it lines would flash which had been invisible before. In samples which were in the direction where increasing concentration was to be expected, these lines appeared in the regular test. This would justify neglecting the flashes which occurred on cleaning the wire.

In Run 101 Samples 2, 3, and 4 gave no indications of calcium, while Samples 10, 11, and 12 gave strong calcium lines with no indication of barium. Behind this sample the agar had the copper color. In Run 102 an attempt was made to see how rapidly a detectable separation would take place. In Sample 5 the lines of barium and calcium appear. Sample 11 was greenish, showing that it contained the copper boundary. It gave the lines of strontium and calcium. Thus about 5 mm. were sufficiently purified so that they showed no lines of the other substance. Calcium appeared throughout. This is additional confirmation of the tendency of the impurities of the agar to collect with the similar substances in the segment.

Table 8

Spectroscopic Analysis of Run 101

Positions	9.0	10.4-10.55	11.65-11.72	11.7-13.5	Flame
Element	K	Ca	Ca b Ba l	Ba	
Sample					
1	l				Pink
2-4			l, b	l	y, G, r
5		b		l	y, G, r
6-9		b	b, l	l	y, G to g, r
10-11		b	b		y, g, r to R
12		b	b		y, R
13		f	f		y, r (agar green)
14-16		f	f		Cu green, o

Spectroscopic Analysis of Run 102

Positions	9.0	9.7-10.3	10.4-10.55	10.7-10.75	11.65-11.7	11.7-13.5	14.5	Flame
Elements	K	Sr	Ca	Sr (Ba, Ca)	Ca b Ba l	Ba	Sr	
Sample								
1.....	l							Pink
2.....	l				f			p, r
3.....	l		f	f	f			p, y, r
4.....	l		f	f	f			p, y, r
5.....	f		b	l	l	l		y, g, r
6.....		f	b	l	l	l	f	y, g, R
7-9....		l	b	l	b	l	l	y, g, R
10.....		l	b	l	b	f	l	y, r
11.....		l	b	l	b		l	y, r (agar green)
12-13...		f	l	l	fb		f	Cu g, y, r

b = band l = line f = flash or faint

The flame tests were made when the samples were taken. The letters represent the colors. Capital letters indicate more intense flames than usual.

Table 9

Spectroscopic Lines of Alkaline Earth Chlorides

	Color	Position	Wave Length[32] (Angström Units)
$CaCl_2$	Red	10.4 -10.55	6265 6202
	Orange	10.75	6181
	Green	11.65-11.72	5543 5517
$SrCl_2$	Red	9.8 - 9.9 9.95 10.0 10.15 10.3	6694 6664 6597 6464 6351
	Orange	10.7 -10.75	6060 6032
	Blue	14.53	4607
$BaCl_2$	Red	10.35	6497 (?)
	Orange	10.73	6141
	Green	11.70 12.1 12.4 12.68	5535 5313 (?) 5242 5136
	Blue Green	13.55	4934
Na.....	Yellow	11.0	5896 5890

[32] "Handbook of Chemistry and Physics," 9th Edition, Chemical Rubber Publishing Co., Pg. 567-72.

DISCUSSION

As soon as the method had been developed sufficiently, attempts were made to separate the isotopes of chlorine. The analytical methods were not closely studied until after it had been proved possible to secure samples for analysis. Due to the small size of these samples gravimetric analysis would not yield the highest precision, even though the methods for the determination of atomic weights were used. The mass-spectrograph offers the possibility of detecting slight differences in atomic mass with small samples. The further study of the gravimetric methods of analysis has been postponed until this instrument has been assembled by Dr. Eric Jette. If it proves applicable the results will be far more accurate than the spectroscopic methods of analysis used with the alkaline earths.

The separation of barium and strontium where the run was only 200 per cent. of the unit length, and the better separation of barium and calcium where the run was about 400 per cent. of the unit length, will help in estimating the length of run to be tried in any future experiments. If chloride ions, hydrated with two molecules of water, have a difference of mobility as calculated, runs of 30 ft. should correspond to 200 per cent. of the unit length for a 2 in. segment, and 60 ft. to 400 per cent. Both of these lengths of run have been attempted using sodium chloride as the source of isotopic ions. The results of these experiments may be masked by the accumulation of chloride, as was discovered in the subsequent runs with the halides.

At first it was thought that the impurities in the agar gave promise of helping to prevent the loss of the materials of the experiment. Instead, they are the greatest hindrance to successful separation of substances similar to them. Calcium and strontium, and bromide and iodide cannot be classed as inseparable until they have been tried in agar free from impurities of similar nature, or until they have been determined separately in the analysis of resulting samples. But until proved necessary it seemed a needless precaution to purify the agar, since the salts subsequently to be introduced would bear the same relation to the agar as the impurities removed.

Another source of inefficiency in separation was the time which elapsed while re-filling the tube, when no current was flowing. The actual labor of emptying and filling the tubes required from one to two hours, depending upon the difficulties and delays encountered. Another period of one to three

hours was required for the hydroxide jelly to set firmly enough to permit the addition of the electrode solutions. The results of several days electrolysis should not be completely destroyed by a few hours of diffusion, but this effect may be relatively great. In the design of any method which would permit of continuous electrolysis the experimental difficulties seem great, so that a further test of the method as now used would seem desirable.

Chloride and iodide have been separated by the same method that was applied to the isotopes. This shows that the method is applicable where the mobility difference is of the same order as may be expected in the case of isotopes. It does not show whether or not the properties are so adjusted naturally as to cancel the effects tending to produce separation. Unless this is the case it would seem that the moving boundary method, especially if it is modified in the indicated ways, should separate isotopes.

SUMMARY

1. The method of moving boundary has been modified by the use of two boundaries between ions of the same electrical charge.

2. The following pairs of ions have been separated:

Iodide and thiocyanate Barium and calcium	Separation practically complete
Barium and strontium Iodide and chloride	Separation only partial

3. The percentage difference in mobility of the ions that have been separated has 1.5 per cent. as its lower limit. This approaches the order of percentage difference which may be expected with isotopes.

VITA

James Frederick White was born in Berea, Ohio, on August 20, 1899. He attended the public schools and High School of this village. After his graduation from High School in 1916 he entered Baldwin-Wallace College and in 1920 received the degree of A.B. cum laude. In 1922 he received the degree of M.A. from Columbia University.

He was an Assistant in the Department of Physics of Columbia University for the year 1920-1921. Since then he has been Fellow, and Tutor, in the Department of Chemistry of the College of the City of New York. Recently he was appointed Professor of Chemistry at Soochow University, Soochow, China.

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